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RATE CONSTANTS FOR THE REACTION OF PO (v = 0) AND PO (v = 1) RADICALS WITH OXYGEN

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Laser-induced fluorescence (LIF) has been used to probe vibrational state population of PO radicals generated by CO_2 laser photolysis of dimethyl methylphosphonate. PO radicals in vibrational levels up to v = 3 have been detected. The population ratio determined for v = 0 and v = 1 is consistent with a vibrational temperature of 1000 K. LIF monitoring of the decay of PO radicals in the presence of an excess of oxygen has allowed determination of the rate constants for reaction of PO (v = 0) and PO (v = 1) with O_2. The measured rate constants for both these reactions are 1.5×10^{-11} cm^3/molecule/s or about 1/25 the hard-sphere collision rate. Potential laser photofragmentation/LIF detection schemes for organophosphonates should accordingly incorporate no more than 10 ns between photolysis and probing for PO radicals.

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PREFACE

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RATE CONSTANTS FOR THE REACTION OF PO (v = 0) AND PO (v = 1) RADICALS WITH OXYGEN

1.   INTRODUCTION

For possible application to class identification of organophosphonates, a UV laser photofragmentation/laser-induced fluorescence (LIF) detection scheme has been studied by Long, Sausa, and Miziolek whose results have been recounted in several recent publications.[1-5] The laser photofragmentation approach uses a focused excimer laser (at 248 or 193 nm) to photodissociate the organophosphonate, and the resultant PO radicals are detected by LIF using a second (unfocused) laser beam whose wavelength is resonant with the strong PO $A^2\Sigma^+ - X^2\Pi$ transition with (0,0) bandheads near 246.3 and 247.7 nm. Many important parameters in this scheme have been determined by these authors: laser power dependence of the fragmentation process, radiative lifetime of the PO A state, rates of quenching of the A state by the atmospheric constituents nitrogen and oxygen, internal state distributions of the PO radical fragment, and pressure dependence of the photofragmentation process, as well as the rate constant for reaction of PO with oxygen.

Because the goal of the work of Long et al.[1,2] was to evaluate this technique for application under ambient conditions, an accurate determination of the rate constant for the PO + O_2 reaction is important. However, the measurement Long et al.[3,4] obtained contradicted two recent prior measurements. Aleksandrov, et al.[6] first extracted a rate constant, $k = 2 \times 10^{-13}$ cm^3/molecule/s, which they attributed to the PO + O_2 reaction in a discharge flow system. Using a microwave discharge in argon containing dimethyl methylphosphonate (DMMP) to generate PO, Wong et al.[7] monitored PO via LIF in the $B^2\Sigma^+ - X$ transition near 325 nm to measure a rate constant of $k = 2 \times 10^{-13}$ cm^3/molecule/s, which is in good agreement with the earlier Aleksandrov experiment.

The work of Sausa, Miziolek, and Long,[3,4] who used a focused KrF (248 nm) laser to photodissociate DMMP and LIF in the A-X transition to monitor PO in the presence of O_2, yielded a rate constant of 1×10^{-11} cm^3/molecule/s, 50 times faster than the measurements using the flow discharge systems.[6,7] An abiding question in the excimer laser study is whether the focused 248-nm laser might generate oxygen atoms by multiphoton-induced photochemistry in O_2, thus confusing the issue of which species actually accounted for the reactive decay of PO.

A technique for photolytic generation of PO in the presence of O_2 without generating oxygen atoms is required to eliminate this problem. This technique is supplied in the present work by using a CO_2 transversely excited atmospheric

(TEA) laser to produce PO by IR multiphoton dissociation (IRMPD) of DMMP. The IRMPD of DMMP in a molecular beam has been studied by Chou, Sumida, and Wittig, who determined the nascent PO product state distributions by multiphoton ionization of PO.[8,9] The effective vibrational temperature was approximately 1000 K, placing the PO (v = 1) population at 17% that of PO (v = 0).

In this report, we present the results of our measurement of the reaction rate of ground vibrational state PO with O_2 using IRMPD of DMMP to generate PO. Because this photolysis technique generates vibrationally excited PO, we have been able to measure the rate of the reaction of PO in its first excited vibrational level, PO (v = 1), with O_2. Prior to discussion of the reaction rate measurements, we present data on the IRMPD of DMMP.

2.   EXPERIMENTATION

The experimental arrangement used in this report was similar to that used by Long et al. in the excimer laser photodissociation studies.[1-4] As depicted schematically in Figure 1, it incorporated a Tachisto 555 or Lumonics 820 CO_2 TEA laser for photolysis and a Quanta-Ray Nd:YAG-pumped dye laser system for production of the PO LIF probe laser beam. Either pure DMMP or oxygen containing less than 0.01 torr DMMP flowed through a stainless steel flow system. The approximately 1-in. i.d. stainless steel cell has four windows at right angles. The laser beams passed through opposing 2-mm thick BaF_2 windows while UV Suprasil windows on the other optical ports allowed viewing of the cell interior. PO LIF was collected by a lens system consisting of a 2-in. diameter, 75-mm focal length Suprasil lens and a 2-in. diameter, 200-mm focal length Suprasil lens onto the slit of a Spex model 1870B, 0.5-M monochromator. The dispersed fluorescence was detected either by an RCA C31034 photomultiplier (PMT) or a Tracor-Northern TN-6100 optical multichannel analyzer (OMA). The OMA was used to record spectra of the PO fluorescence while the PMT, whose output was averaged in a PAR model 162 boxcar averager, was used for the kinetics studies. The boxcar averager output was further accumulated and stored in a DEC MINC laboratory computer.

The CO_2 laser output was focused into the flow cell by a 10-cm focal input ZnSe lens; the UV probe laser beam was used unfocused. A master trigger system incorporating several delay pulse generators was employed to control the timing of the laser pulses in these two-laser experiments. A BNC model 7075 digital delay generator provided the critical time delay between the lasers. In the following discussions, "probe laser delay" always refers to the time interval between the initial CO_2 photolysis laser pulse and the UV laser pulse used to probe for the concentration of PO radicals in a given state at a given time after photolytic preparation.
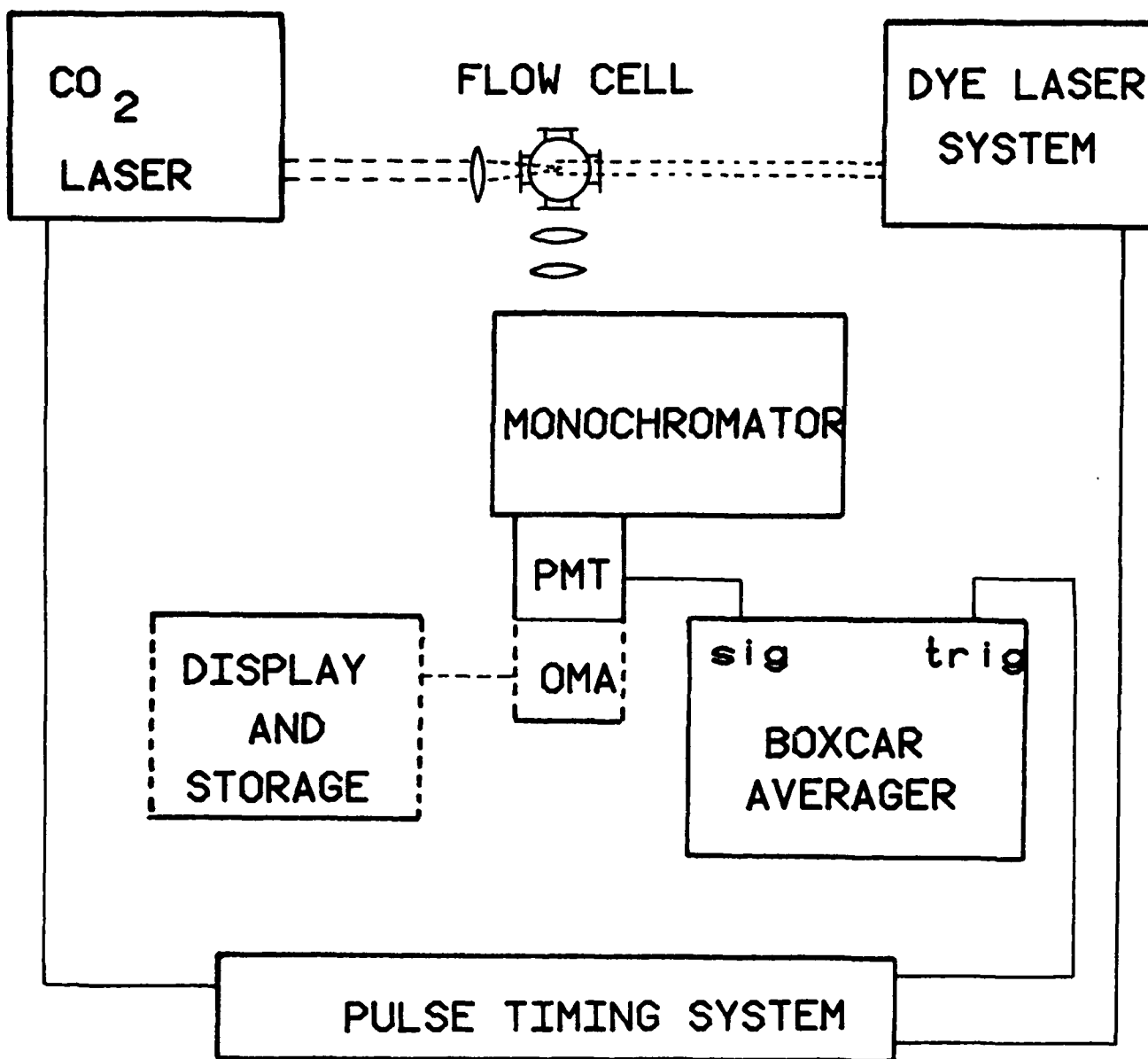
Figure 1. Experimental Schematic.

The CO_2 laser pulse is approximately 100 ns wide with a low intensity tail to 1.5 µs. The pulse was generally used at the 9P(18) line at 1049 cm^{-1} for this work. Absorption by DMMP at this frequency is strong. The UV probe beam has a time width of about 5 ns.

3.   RESULTS AND DISCUSSION

3.1   IR Multiphoton Dissociation of DMMP.

Our observations of the PO radical following its production by IRMPD of DMMP are limited to a determination of the vibrational levels of ground electronic state PO generated and their approximate relative population ratios. A full description of the nascent PO vibrational, rotational, and spin-orbit population after IRMPD of DMMP under collision-free (low pressure) conditions has been reported by Chou et al.[8,9] who used mass spectrometric detection of PO^+ formed by two-frequency, two-photon ionization of PO via its $B^2\Sigma^+ - X^2\Pi$ transition near 325 nm. Where there is overlap between our observations and those of Chou et al.,[8,9] the agreement between the two different studies is excellent.

Because our focus is on determining the rate of reaction of PO with O_2, we naturally operate at pressures where collisions are important. Our kinetics measurements are made under conditions of at least 0.25 torr total pressure and at least 1-µs delay of probe laser after photolysis. Therefore, at a minimum, a PO radical would experience several collisions before detection by the probe laser (collision rate for PO on O_2 is approximately 12 µs^{-1} torr^{-1}), and the nascent rotational and spin-orbit populations would be substantially thermalized during this time. However, vibrational relaxation typically requires several hundred to several thousand collisions. Therefore, vibrational relaxation could occur on the timescale of the reaction between PO and O_2, and it is important to confirm the relative population of the low-lying vibrational levels of PO formed by IRMPD in order to evaluate the extent to which vibrational relaxation (e.g., v = 1 to v = 0) may affect our rate measurements (e.g., where we monitor decay of v = 0).

Figures 2-5 display a series of fluorescence spectra of PO, generated by IRMPD of DMMP, for which the probe dye laser wavelength was set to excite PO via its (0,0), (1,1), (2,2), and (3,3) bandheads in the A-X transition. The wavelengths used for fluorescence excitation and relevant experimental parameters are provided in the figure captions. The appropriate wavelengths to employ for excitation of the various vibrational levels of the A state were extracted from spectroscopic constants supplied by References.[10-12] Similarly, all observed fluorescence features are readily attributable to PO A-X (v',v") bandheads by correspondence of the observed wavelengths with those calculated from the relevant spectroscopic constants.[10-12]
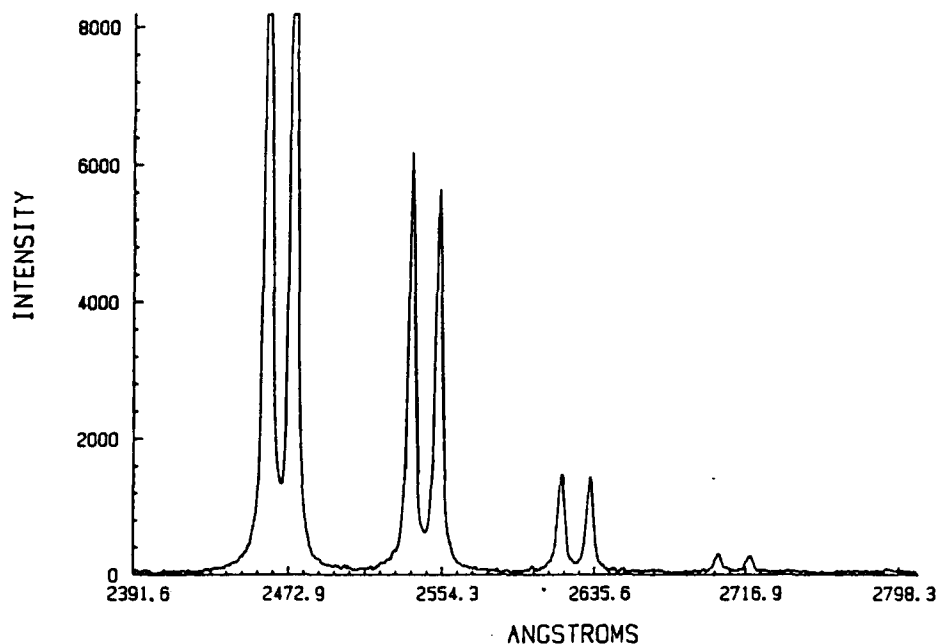
Figure 2.   PO A-X LIF Excited Via the (0,0) Band.
Excitation wavelength: 246.3 nm. CO_2 laser energy: 130 mJ.
Probe laser delay: 4 μs. DMMP pressure: 0.4 torr.

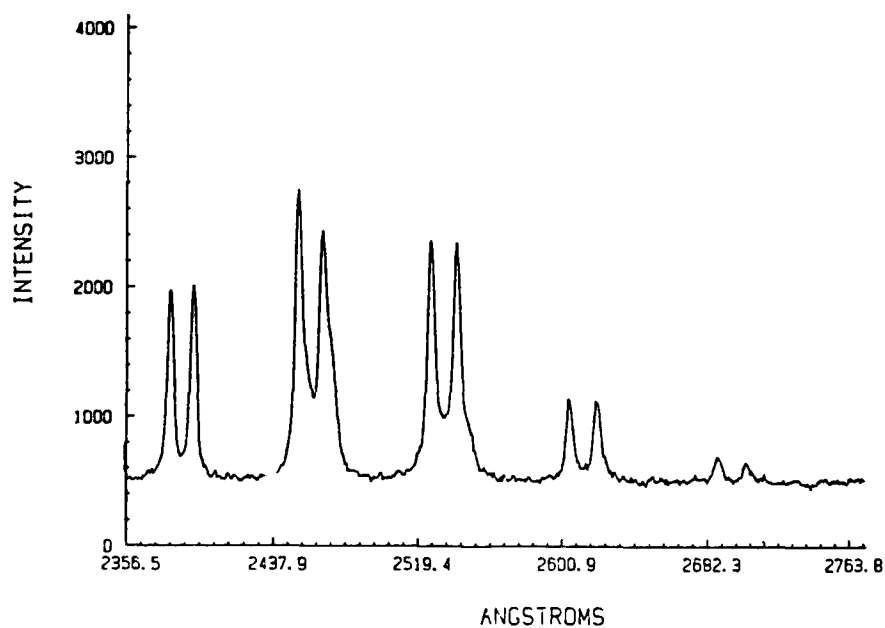
Figure 3.   PO A-X LIF Excited Via the (1,1) Band.
Excitation wavelength: 245.3 nm. CO_2 laser energy: 150 mJ.
Probe laser delay: 2 μs. DMMP pressure: 0.4 torr.

Figure 4. PO A-X LIF Excited Via the (2,2) Band.
(2,v") bands are denoted by arrows. See text for explanation of
additional bands. Excitation wavelength: 244.4 nm. CO_2 laser
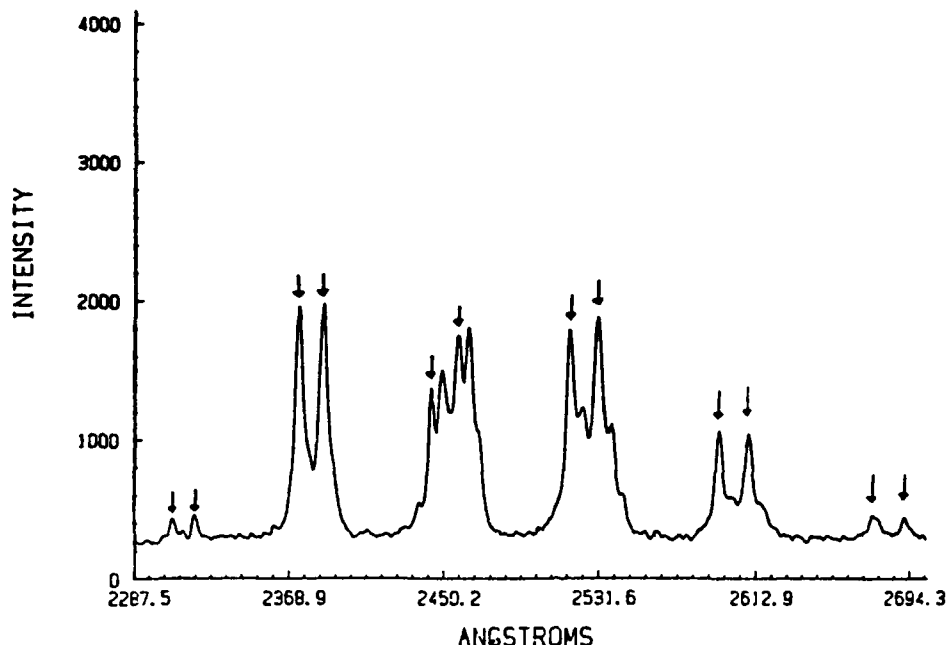energy: 200 mJ. Probe laser delay: 2 µs. DMMP pressure: 0.4
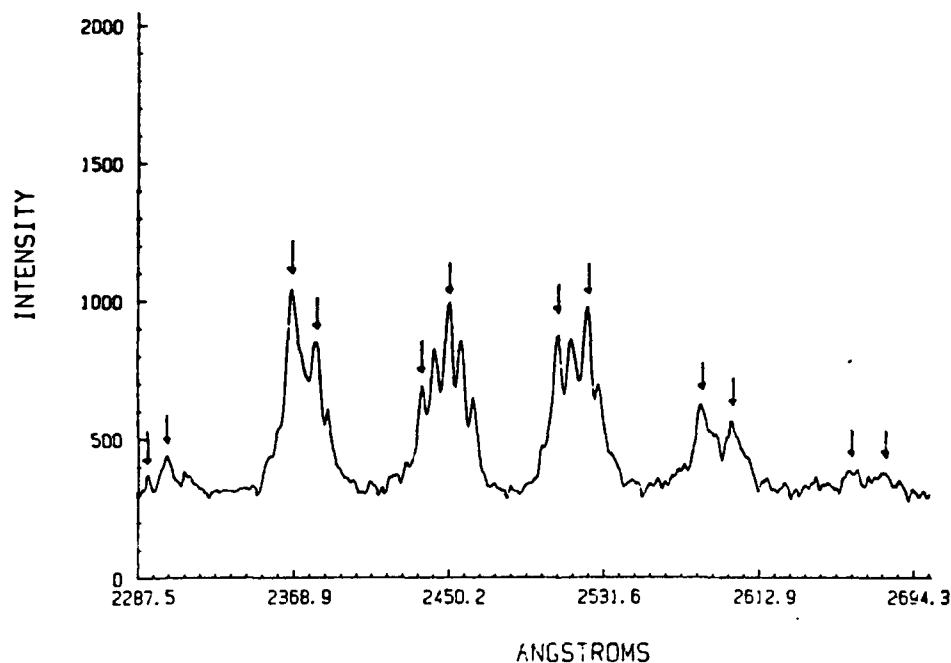torr.

Figure 5. PO A-X LIF Excited Via the (3,3) Band.
(3,v") bands are denoted by arrows. See text for explanation of
additional bands. Excitation wavelength: 243.6 nm. CO_2 laser
energy: 230 mJ. Probe laser delay: 4 µs. DMMP pressure: 0.4
torr.

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As an example, the wavelengths we observe for PO A state v' = 0 fluorescence (Figure 2) are collected for comparison with those of Dixit et al.[10] (observed in a discharge tube) in Table 1. The agreement is good considering the ±0.1 nm accuracy of our measurement.

Table 1. Wavelengths of Bandheads in the A-X $(0,v")$ Progression.

Band	Branch	Ref. 10*	LIF, this work
(0,0)	Q_1, P_1	2463.2	2462.4
	P_2, $^oP_{12}$	2477.0	2475.4
(0,1)	Q_1, P_1	2539.4	2538.1
	P_2, $^oP_{12}$	2554.0	2552.7
(0,2)	Q_1, P_1	2619.7	2617.8
	P_2, $^oP_{12}$	2635.2	2633.2
(0,3)	Q_1, P_1	2705.1	2702.3
	P_2, $^oP_{12}$	2721.5	2719.4

*The wavelengths shown in this column represent the average wavelength of the appropriate bandheads because, with our apparatus, we do not resolve the close-lying Q_1 and P_1 or P_2 and $^oP_{12}$ bandheads.

Some explanation of the structure of the fluorescence spectrum is in order. Because it is a $^2\pi$ state, the lower state in the A-X transition is spin-orbit split into two components, one with $\Omega = 3/2$ lying 224 cm-1 above the $\Omega = 1/2$ component. Accordingly, the vibrational bands in the fluorescence spectra appear as widely spaced doublets with the longer wavelength member of each doublet corresponding to fluorescence to X, $^2\pi_{3/2}$. As Table 1 indicates, bands in the A-X system actually form heads in four branches. However, the heads associated with the Q_1 and P_1 branches (due to A-X, $^2\pi_{1/2}$) and those in the P_2 and $^oP_{12}$ branches (due to A-X, $^2\pi_{3/2}$) are too close to be well-resolved with our resolution (0.15 nm), and the bands appear as widely spaced doublets.

It may be noted that, while the fluorescence spectra generated by exciting in the (0,0) and (1,1) bandheads (Figures 2 and 3, respectively) consist of only a single series of vibrational bands (as doublets) due to v' = 0 and v' = 1,

respectively, the spectra arising from (2,2) and (3,3) bandhead excitation (Figures 4 and 5) have features in addition to the $v' = 2$ and $v' = 3$ progressions. These additional bands are due to spectral overlap of the (2,2) and (3,3) bandheads and high K (rotational) transitions of the lower (v',v'') bands of this system. Thus, excitation in the (3,3) bandhead yields fluorescence not only from $v' = 3$ but also from $v' = 2$ and $v' = 1$ of the A state.
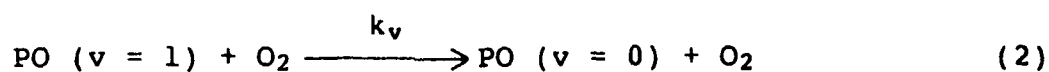
These spectra demonstrate that vibrational levels from $v'' = 0$ to at least $v'' = 3$ of the ground electronic state of PO are generated by IRMPD of DMMP. To extract an estimate of the vibrational temperature of the PO radical fragment, we measured the relative population of $v'' = 0$ and $v'' = 1$. With CO_2 laser energy of 3.5 mJ/pulse and a DMMP pressure of 0.35 torr, the fluorescence signals monitored at a (0,1) bandhead following (0,0) excitation and at a (1,2) bandhead following (1,1) excitation were ratioed. (The monochromator was set to pass the appropriate, monitored bandhead and the signals measured using the PMT/boxcar averager system. The probe laser delay was such that rotational relaxation was complete.) The observed signal ratio was scaled according to the different Franck-Condon factors for the relevant bands:[13] (0,0), 0.696; (0,1), 0.244; (1,1), 0.280; (1,2), 0.318. This scaling yields a ratio of $v'' = 1$ population to $v'' = 0$ population of 0.17. Using this population ratio with the PO vibrational spacing of 1230 cm^{-1} yields a vibrational temperature of approximately 1000 K. This result is identical to that obtained by Chou et al.[8,9] who detected PO by resonant two-photon ionization at low pressures in a time-of-flight mass spectrometer.

3.2   Reaction of PO with Molecular Oxygen.

Having established that IRMPD of DMMP generates PO in several low-lying vibrational states with a characteristic temperature of approximately 1000 K, we may discuss measurement of the rate constants for the reaction of PO ($v'' = 0$) and PO ($v'' = 1$) with O_2. In these studies, we operate under conditions of excess oxygen so that the biomolecular PO + O_2 reaction becomes pseudo-first order. Because the LIF signal of PO is directly proportional to its concentration at the low laser intensities we employ, exponential decay of the LIF signal with increase in probe laser delay after IR photolysis is expected: I is proportional to $\exp(-k_{obs}t)$, where I = PO LIF signal and the observed pseudo-first-order rate constant $k_{obs} = k_r[O_2]$, where k_r = the bimolecular reaction rate constant and $[O_2]$ is the known O_2 concentration in excess. Thus, the slope of the semilogarithmic plot of LIF signal versus probe laser delay t is the observed first-order rate constant. Further plotting of k_{obs} versus the O_2 concentration over a range of O_2 pressures yields the bimolecular rate constant as the slope.

This approach assumes that the only process that affects the concentration of PO in the probed vibrational state on the time scale of the reaction is the reaction itself. Because the IRMPD generates PO in an array of vibrational states, a potential complication exists due to the possibility of collisional relaxation of vibrational states higher than those being probed. If this vibrational relaxation occurs on the same time scale as the reaction with O_2, the probed vibrational state of PO will be replenished (as well as depleted at $v'' > 0$) as the reaction proceeds.

However, we can show that vibrational relaxation does not significantly perturb our rate constant measurement. For $v = 0$ PO, the pertinent processes are

$$PO\ (v = 1)\ +\ O_2 \xrightarrow{\ k_1\ } products \tag{1}$$

$$PO\ (v = 1)\ +\ O_2 \xrightarrow{\ k_v\ } PO\ (v = 0)\ +\ O_2 \tag{2}$$

$$PO\ (v = 0)\ +\ O_2 \xrightarrow{\ k_o\ } products \tag{3}$$

Processes involving $v > 1$ need not be considered because the population above $v = 1$ is only 3% of the total (at the determined vibrational temperature of 1000 K). The time dependence of PO ($v = 0$) is, according to the above mechanism, given by

$$d[PO(v = 0)]/dt = k_v[PO(v = 1)][O_2] - k_o[PO(v = 0)][O_2] \tag{4}$$

The concentration of PO ($v = 1$) at any time t is readily obtained as

$$[PO(v = 1)] = [PO(v = 1)]_o \exp\{-(k_1 + k_v)[O_2]t\}. \tag{5}$$

Substituting equation 5 with equation 4 yields a differential equation whose solution is

$$[PO(v = 0)] = \left(\frac{k_v[PO(v = 1)]_o\ e^{K[O_2]t}}{K[O_2]} + C \right)\ e^{-k_o[O_2]t} \tag{6}$$

where

$$K = k_0 - k_1 - k_v \qquad (6a)$$

and C is an integration constant.

We can use equation 6 to estimate the effect of vibrational relaxation of $v = 1$ PO on our measurement of the $v = 0$ PO reaction rate. We need only be concerned with relaxation rate constants k_v with values roughly similar to the reaction rate constant k_0, since for $k_v \gg k_0$ and $k_v \ll k_0$, the observed rate constant is not affected by k_v. The slope of a plot of $\ln[PO(v = 0)]$ versus time, according to equation 6, is the observed pseudo-first-order rate constant. The slopes (observed rate constants) for several values of k_v from an order of magnitude below to an order of magnitude above the rate constant we have measured are listed in Table 2. These calculations are for an O_2 pressure of 1 torr and use for k_0 and k_1 our observed rate constant of 0.44 μs^{-1} torr^{-1} (discussed in the following paragraphs). In addition, our observed nascent population ratio $[PO(v = 1)]_0/[PO(v = 0)]_0 = 0.17$ is incorporated.

The calculated rate constants of Table 2 are only slightly different than the assumed accurate rate constant of 0.44 μs^{-1}. This demonstrates that vibrational relaxation causes a minimal perturbation in the observed rate constant. If it is a simple vibration-to-rotation,translation (V-R,T) energy transfer process, as expected, the vibrational relaxation process (reaction 2) would require several hundred to several thousand collisions. Thus, k_v would be much less than our observed reaction rate constant and vibrational relaxation would not affect the rate constant measurement.

Table 2. Dependence of Observed Reaction Rate on k_v According to Equation 6.

k_v	calculated rate constant
0.04	0.434
0.1	0.430
0.4	0.428
1.0	0.436
4.0	0.440

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In measuring the reaction rate for PO (v = 0) with O_2, the output of the Tachisto 555 CO_2 laser [9P(1´ line] was focused (10 cm f.l. lens) into the stainless steel cell through which oxygen containing less than 0.01 torr DMMP flowed. Oxygen partial pressures ranged from 0.25 to 1.4 torr. Concentration of v" = 0 PO was followed by LIF excited at the (0,0) Q_1 bandhead (formed by rotational levels K near 7.5) of the A-X system (246.3 nm). Fluorescence was monitored at the (0,1) bandhead at 255.4 nm. The probe laser pulse energy was typically 0.5 mJ/pulse and applied without focusing. The fluorescence intensity was measured using the PMT/boxcar averager system with digitization and storage of the boxcar output by the DEC MINC computer. Most of our data has been generated using CO_2 laser energies of several tens of milli-joules. Data collected using from 4 to 400 mJ of CO_2 laser energies show that the PO decay rate is unaffected by change in photolysis laser energy.

As noted earlier, the loss of PO v" = 0 in the presence of O_2 was monitored at O_2 pressures ranging from 0.25 to 1.4 torr. Figure 6 presents a typical semilogarithmic plot of PO LIF at 1 torr O_2 pressure versus probe laser delay and demonstrates that the decay of PO concentration is well-described as exponential and pseudo-first order. (The upper curve of Figure 6 shows the time dependence of PO v" = 0 LIF with 1 torr nitrogen, a nonreactive surrogate for O_2, and illustrates that, after initial rotational equilibration, the PO v" = 0 concentration does not vary on the time scale of the reaction with O_2. The line is a least-squares fit of data to 30 μs delay.) The observed pseudo-first-order rate constants determined at each O_2 pressure studied are plotted against the O_2 pressure in Figure 7. The observed rate constant is linearly dependent on O_2 pressure.

The kinetic behavior described by the plots of Figures 6 and 7 indicates that the loss of PO results from a simple bimolecular reaction between PO and O_2. The rate constant we obtain, as determined by the slope of Figure 7, is 1.4 (±0.2) x 10^{-11} cm^3/molecule/s or 0.44 μs^{-1} $torr^{-1}$. This result agrees with that of the earlier excimer laser studies, providing confirmation of both the rate constant measurement and the absence of oxygen atom perturbation of the excimer laser result. The hard sphere collision rate for PO on O_2 is about 12 μs^{-1} $torr^{-1}$; the PO + O_2 reaction is then relatively rapid as approximately 1 in 25 collisions leads to reaction.

To measure the decay of v" = 1 PO in the presence of O_2, we have used the same procedures as discussed for v" = 0 PO except that excitation by the probe occurred at the (1,1) Q_1 bandhead at 245.3 nm and fluorescence was monitored at the (1,0) bandhead at 239.4 nm. In addition, the total pressure of the system was maintained at 1 torr by adding N_2 buffer to minimize decay of PO LIF with time due to diffusion of PO out of the detection region of the cell. Figure 8 provides a sample

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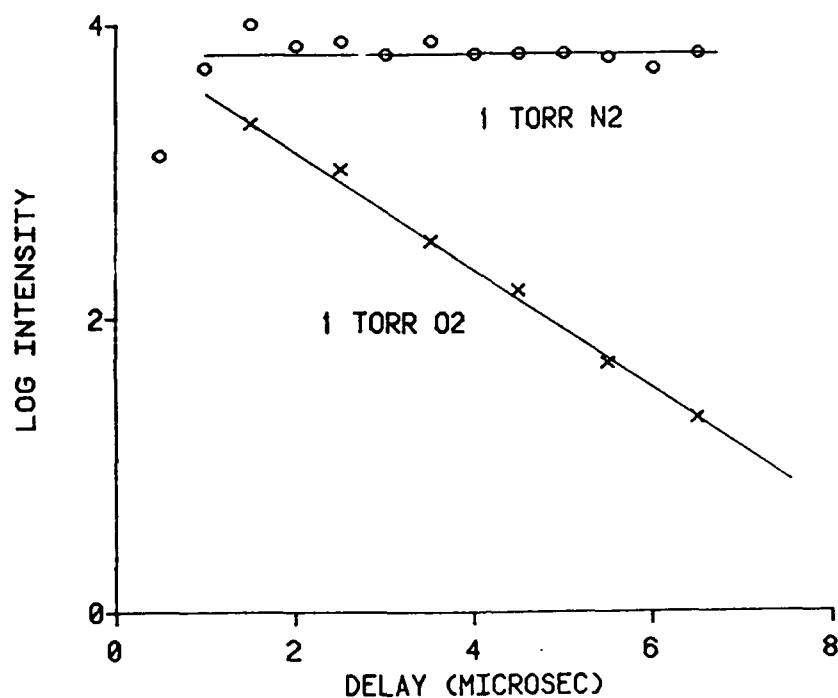Figure 6.   Plot of PO v = 0 LIF Intensity Versus Probe Laser
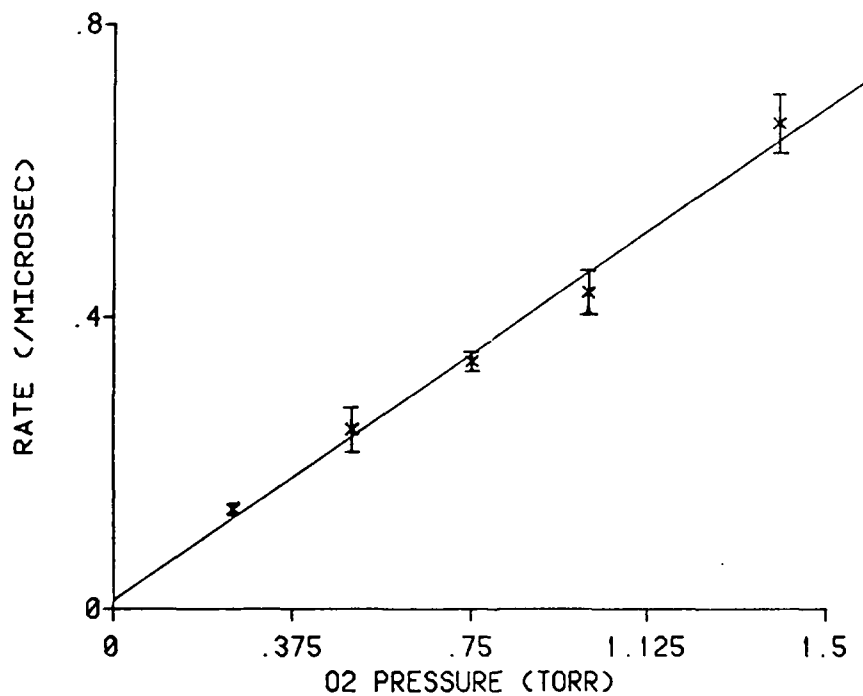Delay at 1 torr O_2.

Figure 7.   Plot of First-Order Rate Constants Versus O_2
Pressure for v = 0 PO.

semilogarithmic plot of PO (v" = 1) LIF as a function of probe
laser delay with N_2 buffer only and with O_2 at 0.45 torr. The
data for three pressures of O_2 (0.25, 0.45, 0.75 torr) as a plot
of the observed pseudo-first-order decay rate versus O_2 pressure
are presented in Figure 9. These plots are very similar to
those for v" = 0 PO. In fact, the measured bimolecular rate
constant for PO (v" = 1) + O_2 is 1.5 (± 0.2) x 10^{-11}
cm^3/molecule/s or identical to the result for PO (v" = 0).

It is not surprising that the additional internal
(vibrational) energy of PO (v" = 1) does not enhance the PO + O_2
reaction rate. Significant enhancements in bimolecular reaction
rates by increasing vibrational energy may be expected when the
vibrationally excited mode is along the reaction coordinate in
the collision complex (i.e., in the bond which breaks). Quite
small reaction rate enhancements are likely when the vibrational
excitation is in a bond that does not break in the reaction.
Our observations show quite simply that the PO + O_2 reaction
follows this expectation.

4.   CONCLUSION

The purpose of the work described herein was to
determine, by independent observation using CO_2 laser IRMPD,
whether the rate constant for the PO + O_2 reaction measured
using excimer laser photolysis[2] was an accurate determination.
The rate constant we find, 1.4 x 10^{-11} cm^3/molecule/s, is in
good agreement with the prior excimer laser-based measurement of
1.2 x 10^{-11} cm^3/molecule/s. There remains the discrepancy of
these measurements with the flow discharge system
measurements[6,7] that derive a rate constant 50 times slower.

Again, the reaction we observe is presumed to be

$$PO + O_2 \longrightarrow PO_2 + O \qquad\qquad (7)$$
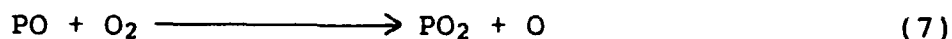
with $\Delta H \approx 1.6(\pm 4.0)$ kcal/mole.[14,15] Although presently undetermined
complications in the reaction mechanism may cause the discrepant
measurements of this rate, the near thermoneutrality of the
reaction coupled with our measured high rate constant implies
the possible establishment of equilibrium between the forward
and reverse reactions in experiments (e.g., the flow discharge
experiments)[6,7] that incorporate a long contact time between
reactants. This problem is compounded by the probable presence
of oxygen atoms (appearing on the product side of the above
equilibrium) in both flow discharge studies. Oxygen atoms are
produced in reference 6 by the PO generation technique, whereas the
microwave discharge in Ar carrier in reference 7 may act as a
windowless Ar lamp generating radiation ~105 nm that could
dissociate some fraction of the reactant O_2. Whether these or
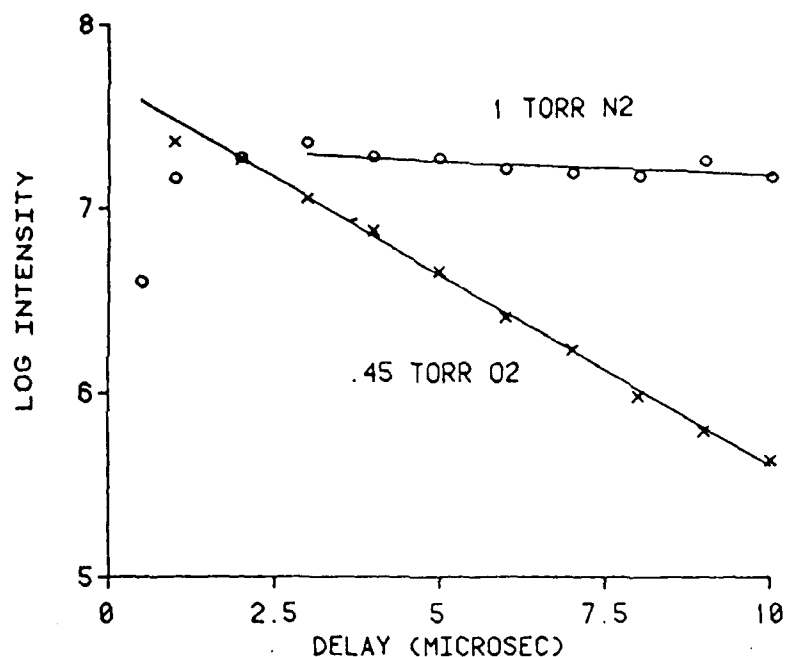other considerations are responsible for the discrepancy would

Figure 8. Plot of PO v = 1 LIF Intensity Versus Probe Laser
Delay at 0.45 torr O_2. Total pressure, buffered by N_2,
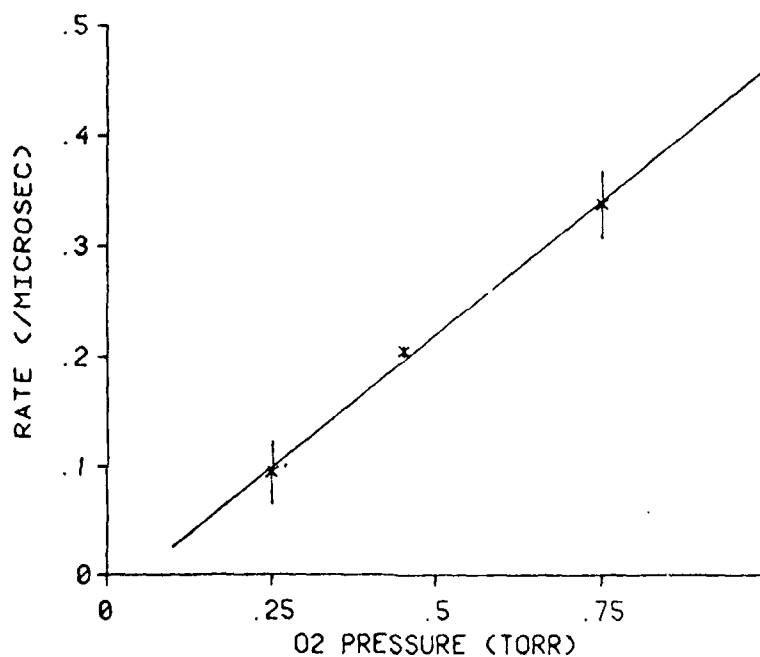is 1 torr. Upper plot is for 1 torr N_2.

Figure 9. Plot of First-Order Rate Constants Versus O_2
Pressure for v = 1 PO.

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require more detailed study of the interactions of various reactive species in the flow discharge experiments.

With respect to detection schemes based on laser photolysis, the measured reaction rate constants impose a limit on the length of delay between generation of PO radicals and their detection by LIF or laser ionization at atmospheric pressure under ambient conditions. In the ambient atmosphere, a PO radical would undergo about two collisions/nanosecond with O_2. Because the PO + O_2 reaction occurs at about 1/25th the hard sphere collision rate, the PO concentration would be at its 1/e value in about 10 ns. Therefore, the PO probe laser pulse should interrogate the detection region within 10 ns of the photolysis laser pulse. Clearly, it would be most advantageous if a single laser pulse were used to perform photolysis and detection where possible.

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